MECHANICAL INTERLOCKING OF ADHESIVE BONDS TO CCA-TREATED SOUTHERN PINE—A SCANNING ELECTRON MICROSCOPIC STUDY

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ABSTRACT

New adhesively bonded products made from lumber, veneer, flakes, and fibers that are protected from biological deterioration can play a prominent role in the marketplace if difficulties in bonding preservative-treated wood can be overcome. The purpose of this study was to demonstrate that bonds of extraordinary integrity can be developed in southern pine treated with chromated copper arsenate (CCA) preservative if a durable adhesive penetrates deeply enough to mechanically interlock within the cellular structure of the wood. Scanning electron microscopy and elemental analysis by energy dispersive spectrometry were used to explore the interfacing of adhesive with the cellular structure of wood treated with CCA preservative. The surfaces of cell lumens were thoroughly covered with hemispherically shaped deposits consisting of mixtures of chromium, copper, and arsenic. The micrographs support physicochemical theories of bonding of metals to microfibrils in cell walls. The presence of insoluble metallic deposits was so pervasive that most opportunities for molecular forces of attraction to act between normally polar wood and adhesive were physically blocked. Our results nevertheless show that adhesion by mechanical interlocking of a phenolic adhesive deep in the cellular structure of CCA-treated southern pine can produce delamination-resistant bonds even after severe cyclic aging.

Keywords: Phenolic adhesives, mechanical interlocking bonds, CCA preservative, southern pine, delamination resistance, SEM (scanning electron microscopy).

INTRODUCTION

During the last 15 years, southern pine lumber production has grown faster than any other segment of the softwood lumber industry. The main driving force has been the market for treated southern pine. Since 1975, the market has more than tripled, and production of treated southern pine now equals almost one-half the total southern pine lumber market. Furthermore, treated southern pine amounts to 80% of the total of treated softwoods in the United States; most of this wood is treated with chromated copper arsenate (CCA) waterborne preservatives (Fuller 1987).

Virtually all growth of the treated southern pine market has occurred without contribu-

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tions from adhesively bonded, treated lumber products. There are two reasons for this lack of development. When wood products are treated with waterborne preservatives after bonding, they degrade from warp, splits, and checks, or they cannot be effectively penetrated with preservative. When wood is treated before bonding, chemicals deposited on the wood surfaces interfere with adhesion to the treated wood. As a result, rigorous requirements for adhesive bond integrity in structural exterior laminates cannot be met with consistency and dependability.

If the difficulties in bonding preservative-treated wood could be overcome, then the potential is great for developing many new adhesively bonded products from lumber, veneer, flakes, and fibers that have been protected from biological deterioration. This report covers a study undertaken at the Forest Products Laboratory to search for ways to overcome adhesive-preservative incompatibility. A series of scanning electron micrographs and data in the literature show physicochemical causes for poor adhesion to CCA-treated southern pine. Another series of micrographs show how an experimental phenolic resin developed bonds of extraordinary integrity to the treated wood despite the many opportunities for interference with adhesion.

The adhesive and techniques used to make the bonds in our study are in preliminary stages of development and are not ready for practical applications. A primary purpose of this work was to demonstrate that mechanical interlocking of adhesive in the cellular structure of wood is a viable approach to effective structural bonding of CCA-treated southern pine.

MATERIALS AND METHODS

Adhesive

The adhesive was made from an alkaline-catalyzed, resol-type, phenol-formaldehyde molding resin. It contained 80% resin solids, 7% of which was urea. The resin was cured with an aqueous ammonium nitrate catalyst (with additives) and heat generated by radio-frequency (RF). Twenty-five parts of catalyst and 20 parts of 50:50 blend of 200-mesh birch wood flour and walnut shell flour were added to 100 parts of the resin. The adhesive used in this study was an experimental preparation and is not available in such form commercially.

The weight-averaged molecular weight of the resin was 7,322 as determined by gel permeation chromatography (GPC). The GPC measurements were carried out on a Waters[2] apparatus, using two Polymer Laboratories 10^4 and 50-nm (500 Å) columns in series, with dimethylformamide containing 2% acetic acid as solvent at a flow rate of 1.00 ml/min. Apparent molecular weights were calculated from a calibration using polystyrene standards.

Treated wood

The wood was 19-mm (1-in. nominal) southern pine lumber that had been pressure treated with CCA preservative by a commercial process. The target retention was 6.41 kg/m^3 (0.4 lb/ft^3). The wood had normal density based on a ring count of 2 to 4 rings per centimeter (6 to 10 rings per inch). The treated wood was conditioned to 12% equilibrium moisture content, then planed to 16-mm (⅝-in.) thickness just before bonding.

Specimen preparation and testing

The delamination specimens were 76-mm- (3-in.-) long sections cut from a 89-mm- (3½-in.-) wide by 305-mm- (12-in.-) long by 95-mm- (3¾-in.) high, six-ply lumber laminate. A laminate was prepared by spreading adhesive on both bonding surfaces in each joint at a rate of 0.39 kg/m^2 (80 lb/10^3 ft^2). Open assembly time was 10 min and closed assembly time, 30 min. The adhesive was cured with a Mann-Russell Model 200 12KVA RF generator operating at 27.12 MHz. The laminates were placed between electrodes so that the cur-

[2] The use of trade or firm names in this publication is for the reader's information and does not imply endorsement by the U.S. Department of Agriculture of any product or service.

rent of the RF field flowed parallel to the plane of the bondlines. The bonds were cured under pressure of 344.5 kPa (50 lb/in.^{2}) with a plate current of 1.0 A with 4.5 kW RF output for 1 min. After bonding, each laminate was cut into three sections for delamination tests.

The specimens were subjected to an extremely severe cycle of vacuum-pressure water soaking with drying (VPSD) treatment. The soaking procedure consisted of submerging specimens in water, applying a vacuum of 84.4 kPa (25 in. Hg) for 30 min, and applying pressure of 516.8 kPa (75 lb/in.^{2}) for 2 h. The drying procedure consisted of placing specimens in a forced-air oven at 71 C (160 F) for 15 h. The entire procedure was repeated four times. Delamination was measured in each bondline on all end-grain surfaces after the final drying step.

Microscopic analyses

High magnification micrographs were obtained with a JEOL JSM-840 scanning electron microscope (SEM). Semiquantitative elemental analyses were made with a Tracor Northern TN-5500 energy dispersive spectrometer (EDS). Wood surfaces were prepared for microscopic examination by either microtoming or splitting, then coating with gold for SEM study and with carbon for EDS study.

Low magnification micrographs were made with a Wild M400 Photomakroskop using fiber optic incident light. Specimen surfaces were prepared for microscopic study by sanding with progressively finer cutting grit.

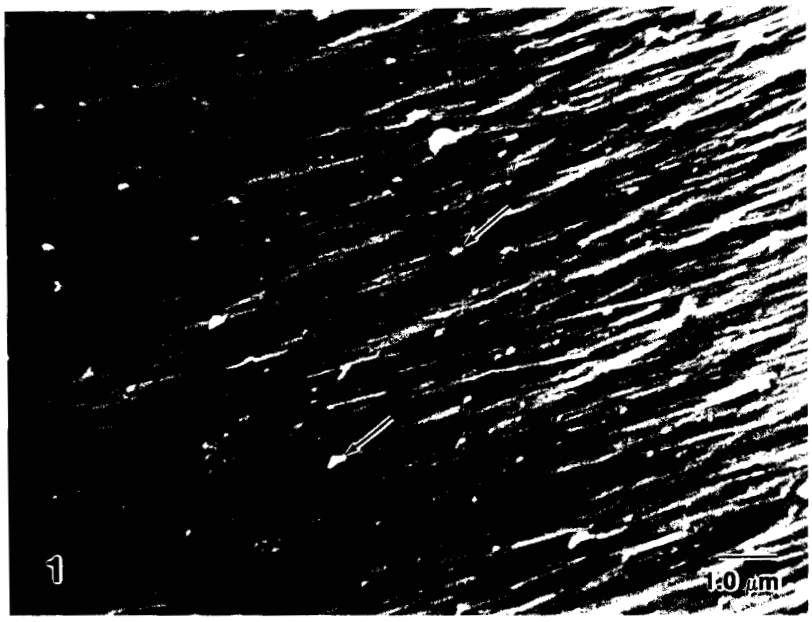
RESULTS AND DISCUSSION

Lumen surfaces of cells

The surface of a cell lumen from untreated southern pine was relatively free of foreign substances (Fig. 1). However, naturally occurring warts in varying sizes were sparsely distributed over the lumen surface. The lumen surface of the same species was dramatically different after the wood was treated with CCA preservative. Figure 2 shows an area of the cell lumen completely covered by a heavy concentration of hemispherically shaped deposits ranging in diameter from around 1.0 μm to essentially invisible at a magnification of 5,000×. In this particular area, very little opportunity existed for the adhesive to make molecular-level contact with lignocellulosic constituents of cell walls without physical blocking by the chemical deposits. Figure 3 provides a perspective for comparing deposit size with the size of a bordered pit aperture. This and other micrographs show that deposits were not large enough to block primary openings between cells. For mechanical adhesion to occur, these openings must remain open to allow flow of resin into lumens six to eight cells deep from where the adhesive is initially spread.

Metal deposits

The chemical and kinetic behavior of copper, chromium, and arsenic in CCA preservatives as these elements fixate to wood, cellulose, and lignin (and respective simple model compounds guaiacol and D(+)-glucose) has been thoroughly studied—most recently by Pizzi (1981, 1982a, b, c). In an earlier series of studies, Dahlgren and Hartford (1972a, b, c), and Dahlgren (1972, 1974, 1975a, b) uncovered many complex kinetic interactions of CCA preservatives with wood. While these authors disagree about the identity of the final equilibrium fixation products and about the relative proportions in which the elements are combined in different chemical species, some important generalizations can nevertheless be made. As the acidic CCA preservatives contact the wood, the pH increases instantaneously as ion-exchange and adsorption reactions occur between the metals and the wood. While the pH is continuously increasing to an eventual maximum level, the main precipitation and fixation of reactants occur. There is ion-exchange fixation of Cu^{+2} to wood and, according to Pizzi (1982c), Cu^{+2} complexes with lignin and cellulose. Chromium arsenate ($CrAsO_4$) complexes with lignin and precipitates on cellulose, whereas $Cr_2(OH)_4CrO_4$ precipitates on cellulose. After reaction with wood, 95% of the CCA system consists of $CuCrO_4$ plus $CrAsO_4$



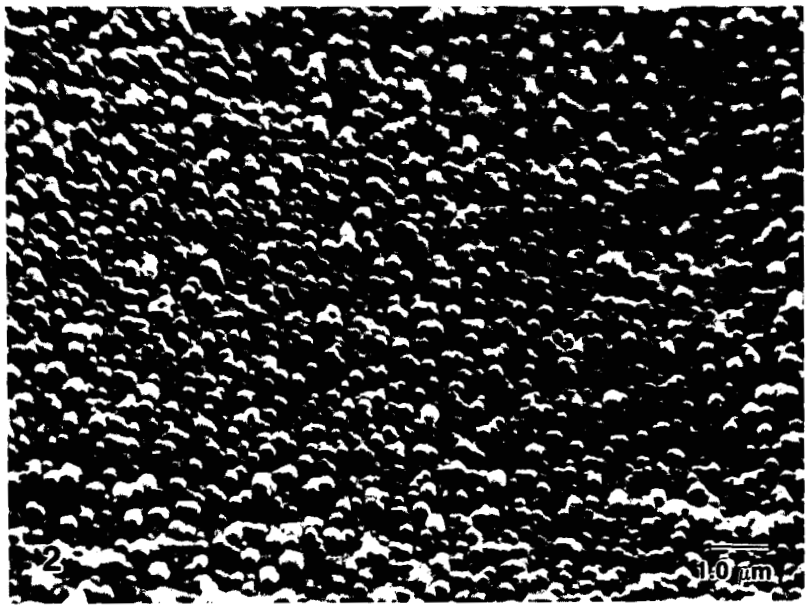
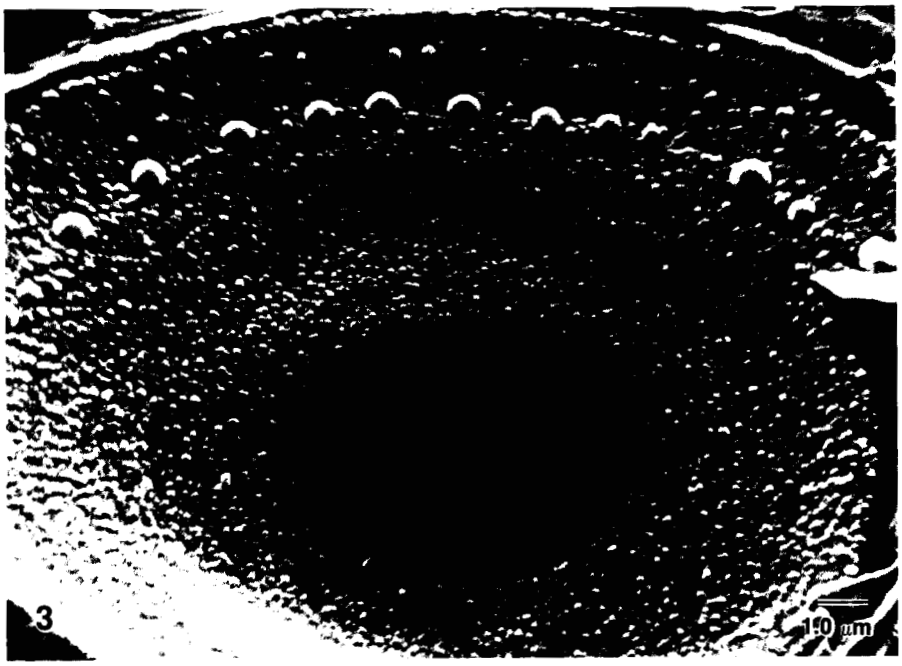


FIG. 1. Surface of cell lumen from untreated southern pine relatively free of foreign substances. Arrows point to naturally occurring warts.

FIG. 2. Surface of cell lumen from CCA-treated southern pine covered with hemispherically shaped deposits, later identified as mixtures of chromium, copper, and arsenic.



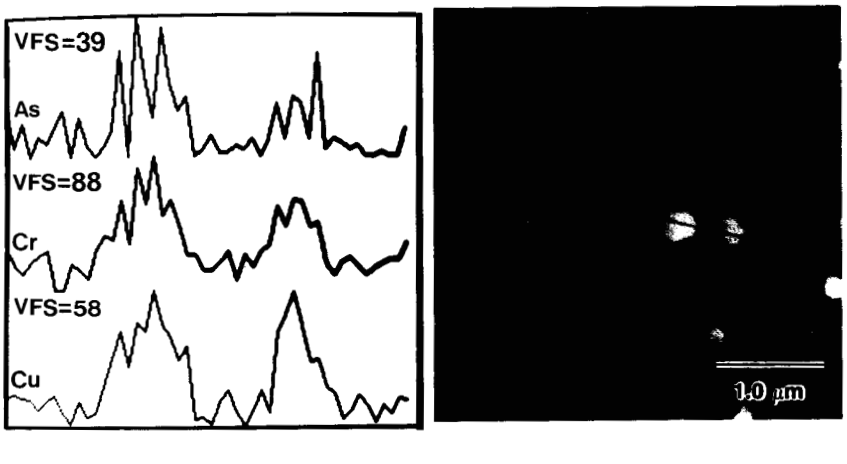


FIG. 3. Pit aperture showing relative size of metal deposits to the opening through which adhesive flowed.

FIG. 4. EDS analysis of arsenic (As), chromium (Cr), and copper (Cu) in two relatively large deposits on lumen surface of treated cell. VFS, vertical full scale in X-ray intensity.

(1982c). According to Dahlgren (1972), all Cr^{+6} is reduced to Cr^{+3}, and the final equilibrium products are $CrAsO_4$, $Cr(OH)_3$, and $Cu(OH)$-$CuAsO_4$.

The elemental analyses by EDS indicated that copper, chromium, and arsenic were all present in precipitates on lumen surfaces and that all these metals were combined within a

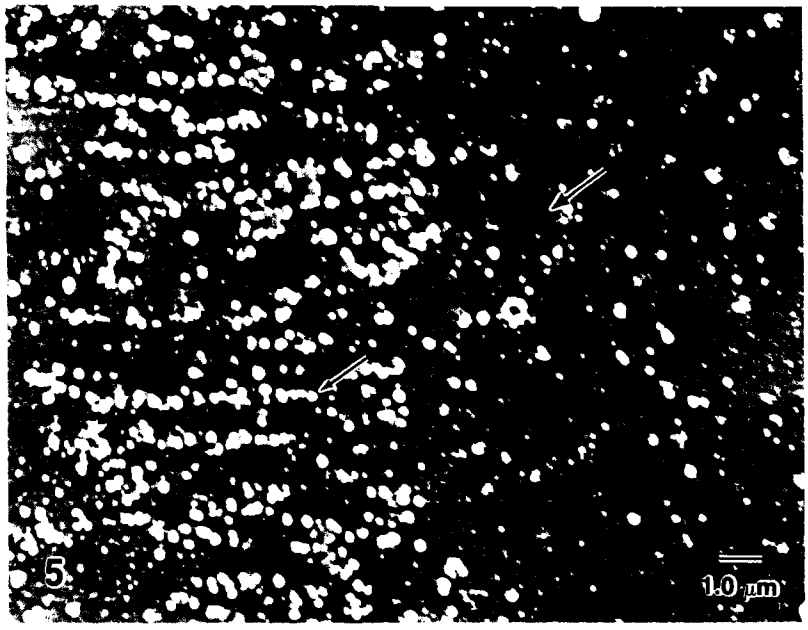
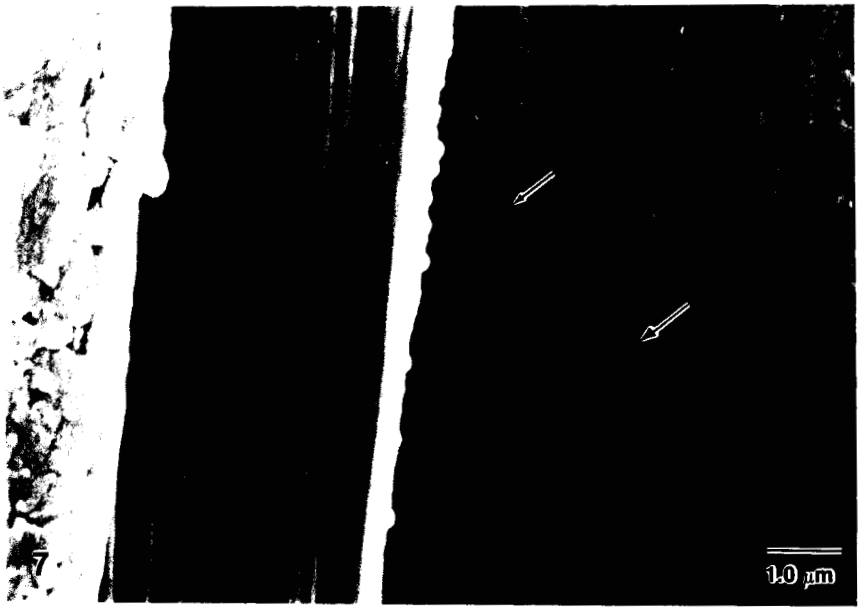


FIG. 5. Parallel alignment of metallic deposits with run of underlying microfibril bundles in cell wall (small arrow). Note direction of striations in lumen membrane (large arrow).

FIG. 6. Lumen membrane with affixed deposits torn away exposing underlying layer of microfibril bundles.



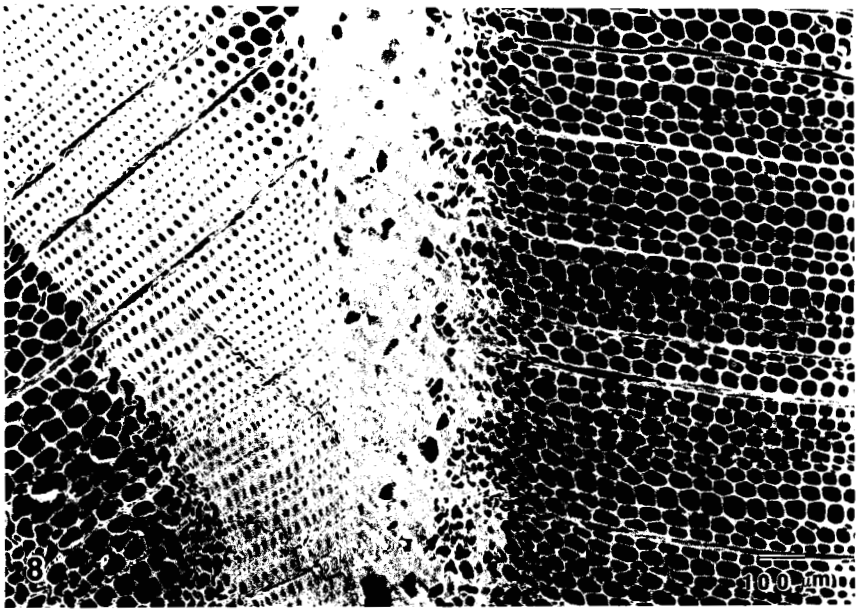


FIG. 7. Impressions of metallic deposits (small arrow) and striations (large arrow) in lumen membrane from underlying microfibrils as they are cast in the solidified adhesive (right). Note tendency of deposits to align with microfibrils in castings.

FIG. 8. Deep penetration of adhesive into springwood and summerwood, which accounted for uncommonly high resistance of wood to delamination in cyclic aging tests.

single deposition. Line scans were passed through two hemispherical deposits—a large one first, then a smaller one (Fig. 4). In the micrograph, the cursor points through the two deposits (Fig. 4). Tracings show the proportions of arsenic, chromium, and copper, as the electron beam encountered continuously varying concentrations of metals as it passed through varying sizes of deposits. The highest peaks, which vertically coincide for all three metals, are the tracings for the larger hemisphere. The second highest vertically coinciding peaks are for the smaller hemisphere. The coinciding peaks show that all three metals were combined within a single deposition. The proportions of metals detected in the first deposit, equated to 100%, were 43% arsenic, 33% chromium, and 24% copper. The proportions of metals in the second deposit were similar.

Using X-ray photoelectron spectroscopy and diffuse reflectance Fourier transform infrared spectroscopy, Ostmeyer et al. (1989) offered evidence that components of CCA preservative form chemical bonds with the aromatic ring of lignin and the carbonyl groups present in wood. In comparison with one- and two-component preservatives that had no marked effect on decrease of aromatic or carbonyl groups, all three components of CCA apparently were required for reactions to take place with these groups. The authors could not determine from the infrared spectra whether or not the metals reacted with carbohydrates.

Figures 5 and 6 show attachment of metallic precipitates to microfibrils. Figure 5 shows single-file alignment of deposits parallel to the striations in the lumen membrane, which were produced by the underlying bundles of microfibrils. In Fig. 6, the lumen membrane (with affixed deposits) was peeled away to reveal more clearly the microfibrils of the underlying layer. High magnification (99,000X) transmission electron microscopic (TEM) examinations by Chow et al. (1973) showed that the distribution of fine deposits of metals is clearly dictated by the run of cellulosic microfibrils. The TEM showed the surface of each microfibril in the secondary wall was coated by a layer of metallic deposits about 1.5 to 2.0 nm thick.

Mechanical interlocking of adhesive in wood

Phenolic wood adhesives form the most durable bonds to wood because they readily penetrate the wood's structure and cure into a thermoset material that is highly resistant to water and heat. Phenolic resins are rich with polar hydroxyl groups that can form hydrogen bonds with polar functional groups on lignocellulosic constituents in cell walls. However, in view of the fixation of insoluble metallic complexes to cell walls, functional groups that might have been available for hydrogen bonding or perhaps covalent bonding on untreated wood simply are not available on treated wood because these sites are physically blocked and chemically tied up in metal complexes. Thus, the only remaining opportunity for effective bonding is through mechanical interlocking of adhesive deep within the wood's structure.

Figure 7 shows how a low-molecular-weight phenolic resin interfaced with the deposit-covered surface of a cell lumen. The dark area on the right half of the micrograph is the cured phenolic resin. While liquid, the resin made intimate contact with the cell wall; when the resin solidified, the cell wall left impressions of the protruding hemispherical deposits and microfibrillar bundles in the resin. An edge view of the lumen membrane with its deposit-covered surface is visible at the center of the micrograph. The cell wall was torn away to reveal impressions of deposits in the solidified resin. In the process of removing the cell wall, adhesion between resin and cell wall was not great enough to cause failure of the cell wall. Actually, there was no evidence of cell-wall failure from a penetrating resin or physicochemical bonding—merely evidence of intimate contact of the resin with the walls. Yet, as Figs. 8 to 11 show, this phenolic resin made excellent bonds to the CCA-treated wood such that no delaminations occurred in the bondlines, even after four cycles of severe VPSD.

Figures 8 to 10 show bonds to CCA-treated

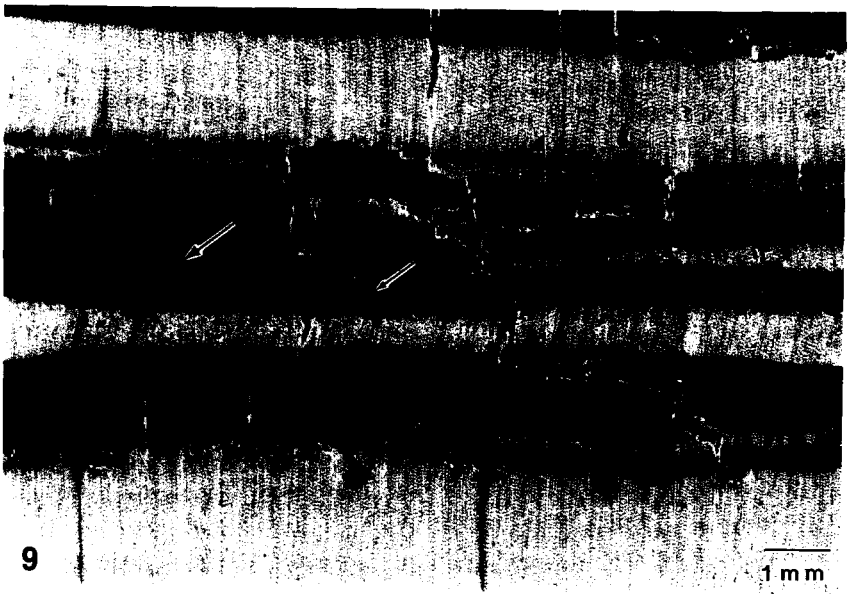


FIG. 9. Bondline (small arrow) showing such high resistance to delamination that rupture occurred through high-density summerwood bands (large arrow). Note deep penetration of adhesive.

FIG. 10. High-integrity bondline (small arrow) showing rupture within wood (large arrow) adjacent to bondline, but never within bondline.

southern pine in a six-ply lumber laminate. Figure 8 shows a cross section of a typical bondline where thick-walled, high-density summerwood in one adherend was bonded to thin-walled, low-density springwood in the other adherend. Adhesive penetration was four to six cells deep in the springwood and one to three cells deep in the summerwood. The un-

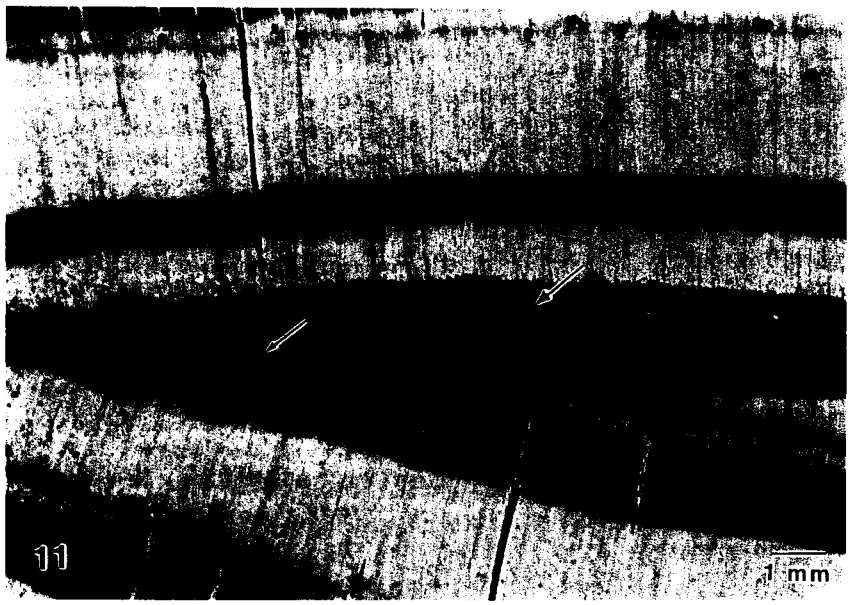


FIG. 11. Juncture of two difficult-to-penetrate summerwood bands (small arrow) where delamination normally would be expected to occur. In this case, high integrity of bond forced rupture to juncture of springwood and summerwood bands (large arrow) above bondline.

commonly deep penetration undoubtedly accounted for the uncommonly high resistance of the wood to delamination.

Figure 9 shows a bondline of such high integrity that it resisted shearing forces that actually ruptured high-density summerwood bands both above and below the bondline. After four severe VSPD cycles, none of the bonds in several six-ply lumber laminates ruptured within the bondline. The ruptures always occurred outside the bondline, either at the juncture of the penetrated resin and wood, or well beyond the bondline. Figure 10 shows typical ruptures of wood that occurred near or sometimes at the bondline, but never within the bondline. Figure 11 is a typical example of where two summerwood bands, which normally are very difficult to penetrate with adhesive, were bonded with such high integrity that the rupture occurred far above the bondline at the juncture of springwood and summerwood. When delaminations occur in either untreated or treated southern pine lumber joints, the ruptures almost invariably develop at the junction of two summerwood bands. The reason for failure in most cases is simply inadequate penetration of the summerwood.

CONCLUSIONS

Scanning electron micrographs (SEM) and energy dispersive spectrometry (EDS) analyses showed that cell lumen surfaces of CCA-treated southern pine were thoroughly covered with deposits consisting of mixtures of chromium, copper, and arsenic. The literature indicates that metals are both physically and chemically complexed with lignocellulosic constituents of cell walls. The SEM and EDS analyses support these findings by showing alignment of metal deposits with the microfibrils in cell walls. By virtue of their physical presence, these deposits block most opportunities for bonding by molecular-level forces of attraction between polar wood constituents and adhesive. Our evidence indicates, however, that mechanical interlocking by a deeply penetrating phenolic adhesive can produce delamination-free bonds to CCA-treated southern pine even after severe cyclic aging tests.

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